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MULTILAYER SHRINK FILM

5    **MOMO (NO)**


This invention relates to a film formed by overlaid layers constituted by thermoplastic polymers of different natures, wherein at least two layers are constituted by a polyamide.

10   Said film is heat shrinkable, being biaxially oriented. It is also perfectly transparent after shrinkage, and has excellent mechanical characteristics and barrier properties to gases, in particular oxygen.

The film according to the invention is therefore suitable for the packaging and storage of perishable food and non-food products.

15   The packaging of perishable foodstuffs has formed the subject of countless research and development projects for years, relating both to the packaging materials and the techniques used.

Especially as regards the field of fresh and processed meat, cheese, fish and other perishable foodstuffs, research has focused on producing packaging

20   materials which basically offer the following performance:

- a high barrier to oxygen, steam and flavourings, which increases the life of the packaged product;

- good mechanical characteristics, so that the contents are protected during transport and can be packaged with automatic machinery;

25   - optical characteristics of transparency and gloss, so that the appearance of the product does not deteriorate and attractive packs are obtained;

- easy sealing to close the wrapping and good strength of said welding;

- good adherence of the wrapping to the contents for various reasons, including preservation of the product.

The use of polymer film has solved many of these problems. In practice, the intrinsic characteristics of the individual polymers are combined to produce a film consisting of a number of laminated or coextruded layers, with the result that the final properties of the multilayer film are the sum of the characteristics of the individual layers.

It is also necessary for the various layers of said multilayer film to adhere well to one another.

The prior art relates to the production of multilayer shrink films wherein the middle layer, which acts as a gas barrier, can be constituted by polyvinylidene chloride copolymer (PVDC), while the outer layers are generally made of polyolefins.

This type of structure is very common, and has been used for many years.

One reason why the barrier layer is positioned in the middle of the laminate is that said layer is usually constituted by a polymer with a high Young's modulus, whereas the polymers that constitute the other layers have a low modulus. If said barrier layer were positioned asymmetrically in relation to the other layers, the laminate would curl as a result of the greater membrane tension exerted.

The polymer that constitutes the barrier layer, in addition to having a high modulus, normally melts at a higher temperature than the polymers that constitute the other layers, and the fact that said barrier layer is located in the interior of the laminate constitutes a problem as regards welding.

To eliminate this drawback and give the film greater mechanical strength, and especially abrasion and puncture resistance, the technique of selective crosslinking of the polymers that make up one or more layers is used. Said

technique makes said polymers partly unmeltable, and in any event increases their melting point. Melting of the layers which come into contact with the heating plates during welding is consequently prevented by crosslinking them.

More recently, polyvinylidene chloride copolymer has been partly replaced by another polymer with barrier properties, namely ethylene/vinyl alcohol copolymer (EVOH).

These shrink film structures usually comprise EVOH in the middle layer, sandwiched by polyolefins in the outer layers. Adherence between the various layers can be obtained with the use of special types of modified polyolefins, also called "adhesives".

Mechanical strength and adherence between the layers can be improved by subjecting the film to irradiation with high-energy particles.

However, although the crosslinking technique solves the welding problem without causing curling and gives the film good mechanical strength, it also gives rise to a serious problem, because it makes the polymers that constitute the film partly unmeltable, and this prevents them from being recycled.

An alternative technique to selective crosslinking, which would solve the welding problems and increase the mechanical strength of the film, would be to use high-strength polymers with a high melting point in the outer layer of the film.

However, in this case the two polymers, ie. the outer and inner ones, differ not only in terms of melting point but also of their modulus of elasticity and degree of crystallinity. As a result, differentiated tensions develop in the structure of the film and the film is pulled to one side, giving rise to the problem of curling already described.

A third problem is loss of transparency (haze) and gloss by the film after shrinking at the application stage. This problem, which adversely affects the final

appearance of the packaging, is mainly due to poor adherence between the layers, which shrink in different ways, and possibly to surface damage caused by the heat applied to obtain the shrinkage.

The above-mentioned problems involved in the prior art are solved by a plastic film
5   conforming to patent application no. MI2002A 002159 filed by the present applicant, namely a multilayer, non-crosslinked shrink film with gas barrier properties, characterised by:

- exceptional mechanical strength,
- easy welding and good welding resistance,
10  - optical characteristics superior to those of ordinary products on the market,
- little or no curling, despite its asymmetrical structure,
- good shrinkage characteristics,
- good adherence to the packaged contents,
- good oxygen and aqueous steam barrier properties.

15  All these characteristics have been obtained without the need to subject the film to ionising radiation treatment, but using a polymer with high mechanical strength and a high Young's modulus, which melts at a high temperature, in the outer layer. In order to eliminate the problem of curling, other layers constituted by polymers with a high Young's modulus are inserted in a suitable position inside the laminate;
20  said layers act in such a way as to balance the effect of the outer layer, thus greatly reducing curling, and even eliminating it entirely in some compositions. However, experiments conducted with numerous compositions demonstrate that these results tend to be somewhat unpredictable. This problem arises when the number of layers with a high modulus is greater than two and, in accordance with
25  said patent application, two or more of said layers are situated inside the laminate on the side of the neutral layer, opposite the side on which the external layer with

the high modulus is located, and said two or more inner layers with a high modulus are adjacent to one another. Under said conditions, a single layer with a high modulus is formed in practice, although its chemical nature is not uniform. The result is that during cooling, said layer with a high modulus, composed of layers

5      with different chemical natures, manifests a high degree of sensitivity to the actual process conditions, with the result that the contractions of the various materials that make up said layer interact with one another in a way which is often unpredictable, and always hard to control. Under these circumstances, curling of the laminate is considerably worsened.

10     The research conducted demonstrates that if a layer of polymer with a low modulus is inserted between two adjacent layers of polymer with a high modulus, the differences between the contractions of the two layers with a high modulus are at least partly absorbed by said layer with a low modulus, with a drastic reduction in the interaction between the two layers with a high modulus, and curling is

15     drastically reduced, or even eliminated, as with the prior art, when the optimum process conditions are present.

When the concepts described above are applied, the research has established some typical preferred configurations.

According to a first typical preferred configuration, the laminate according to the

20     invention comprises seven layers (A, B, C, D, E, F and G), starting with the layer in contact with the product, composed as follows:

- layer A, thickness 20%, welding layer – constitutes the inner part of the wrapping, and can be constituted by ionomers containing zinc or sodium, or a low-density polyethylene, or linear low-density polyethylene (LDPE/LLDPE), or

25     an ethylene or octene plastomer;

- layer B, thickness 10%, first adhesive layer – consists of an adhesive polymer

selected from among ethylene copolymers or terionomers modified with maleic anhydride, or of an EVA/ethylene methacrylic acid copolymer;

- layer C, thickness 15%, first barrier layer (mainly to aqueous steam) – consists of a polyamide polymer selected from among PA 6, PA 6/66, amorphous or aliphatic PA or a mixture thereof, possibly with the addition of terionomers;

- layer D, thickness 15%, second adhesive layer – consists of an adhesive polymer selected from among ethylene copolymers or terionomers modified with maleic anhydride, or of an EVA/ethylene methacrylic acid copolymer, and may be equal to or different from layer B;

- layer E, thickness 15%, second barrier layer (mainly to aqueous steam) – consists of a polyamide polymer selected from among PA 6, PA 6/66, amorphous or aliphatic PA or a mixture thereof, possibly with the addition of terionomers, and may be equal to or different from layer C; alternatively, PVA (polyvinyl alcohol) or PGA (polyglycolic acid) can be used;

- layer F, thickness 10%, third adhesive layer, consists of an adhesive polymer selected from among ethylene copolymers or terionomers modified with maleic anhydride, or of an EVA/ethylene methacrylic acid copolymer, and may be equal to or different from layers B and D;

- layer G, thickness 15%, outer layer and fourth barrier layer (mainly to aqueous steam) – consists of a polyamide polymer selected from PA 6 and PA 6/66.

There is a 5% variability in the thickness of each layer, except for the two outer layers, for which the variability may be up to 10%. This variability is not a tolerance, but a possible choice, depending on the characteristics to be obtained. For example, if the barrier effect is to be increased, the thickness of the barrier layers will be increased, whereas if the laminate is to be balanced better to reduce

curling, the thicknesses of the layers constituted by material with a low Young's modulus will be gauged to distance the layers constituted by materials with a high Young's modulus suitably from one another.

As will be seen, the layer of film which remains on the outside of the packaging is

5    constituted by a polymer with a high modulus and a high melting point, so as to provide high mechanical strength and easy welding, while the inner layer, namely the one in contact with the product, is constituted by an ionomer or another polymer with a low modulus which, in addition to a low melting point to allow welding, also has the property of adhering to the contents of the pack.

10   In the configuration described, there are two other barrier layers (C and E) in addition to the outer layer, which has the function of providing high mechanical strength and forming a aqueous steam barrier.

Layer B (adhesive layer) is positioned between layer A (welding layer) and layer C (barrier layer) because, as said layers consist of polymers with different natures,

15   they would not adhere well, and hazing and loss of gloss would therefore occur during the shrinkage stage.

In view of the chemical compatibility between the three barrier layers C, D and E, there is no interposition of adhesive.

Conversely, layers D and F (also adhesive layers), are positioned between two

20   barrier layers, not with the function of improving adherence, because the two layers have the same chemical nature and are therefore perfectly compatible, but to distance two layers with a high modulus from one another, placing them in a suitable position in relation to the neutral plane, in order to minimise the curling effect.

25   In particular, layer D has the function of reducing the interactions between the two layers with a high modulus (C and E) at the cooling stage as far as possible in

order to limit, if not eliminate the effects of the process variables on the residual tensions.

The film according to the invention is obtained by means of double- or triple-bubble processes.

5    The double-bubble process involves extruding a primary tube comprising said seven layers, cooling it with water at the outlet from the extrusion head (first bubble), and then heating it in suitable ovens with infrared heating elements. When the pre-set temperature is reached, the tube is inflated with compressed air and simultaneously stretched in two directions: longitudinal (MD), namely in the

10   machine direction, due to the effect of the stretching caused by two rollers that rotate at different speeds upstream and downstream of the bubble, and transverse (TD), due to the expansion of the original tube caused by the compressed air blown in (second bubble).

In some cases (triple-bubble process) the tube, flattened by the roller, is

15   subsequently sent to another infrared oven where, being inflated with air at low pressure, it can contract due to the effect of the heat, and may lose some of the shrinkage (third bubble).

The result of said operation connected with the third bubble is partial release of the internal tensions accumulated by the various layers of film, which said tensions

20   may be unevenly distributed between the various layers of the film, and post-recrystallisation.

The stretching and inflation ratio in the first bubble is substantially between 1:3 and 1:5 in the machine direction (MD) and between 1:3 and 1:4.5 respectively in the transverse direction (TD).

25   This means that a primary tube thickness of between 300 and 1300 $\mu$m produces biaxially oriented film with thicknesses substantially between 20 and 60 $\mu$m,

depending on the stretching percentages applied.

When the film thus obtained is heated at a temperature close to the orientation temperature, it tends to return to its original dimensions, namely to shrink.

Tests conducted on packaging made with laminates according to the invention demonstrate that the film adheres perfectly to all types of content, whether it has a very greasy surface, like processed meat such as smoked bacon, or has very irregular, hard surfaces with sharp edges, like ripe parmesan cheese with rind.

In the case of smoked bacon, the film adheres well to the product after shrinkage without the formation of microcavities containing air, which can cause oxidation of the product, especially if it has a high animal fat content.

In the case of ripe parmesan cheese with rind, the shrinkage percentage and shrinkage force of the film developed during the packaging operation enable the film to be wrapped with care and precision, regardless of any irregularities of shape, without leaving cavities, and thus developing very close contact with the contents.

In practice, it has also been found that said adherence of the film to the contents remains intact for up to twelve months, a period which is generally longer than the usual shelf lives guaranteed by the suppliers of these types of foodstuffs.

Said adherence to the packaged product depends on the surface tension of inner layer A of the film in relation to the nature of the surface of the contents, and on the force with which the film shrinks.

The first phenomenon takes place on a "micro" scale, and relates to the state of the two surfaces (film / product), ensuring good adherence even in the presence of adverse factors like animal fat, which can prevent good adherence.

The second phenomenon takes place on a "macro" scale, and relates to the force with which the film shrinks and consequently adheres to the contents (shrinkage

force). It is directly associated with the characteristics of the polymers used in its structure.

In biaxially-orientated shrink film, the parameter directly associated with the shrinkage force is given by the yield point: the higher the yield point of the polymer

5    at ambient temperature, the higher the shrinkage force developed by the film oriented at the application stage.

If the modulus of elasticity is high, the adherence of the film to the contents tends not to relax with time.

In the case of the structure according to the invention, the polyamides used have

10   yield points greater than 25 MPa and moduli of elasticity greater than 3500 MPa. Both are high values, not only in absolute terms, but also when compared with those of the alternative barrier polymers (EVOH, PVDC) used for similar biaxially-oriented films. In the case of these latter polymers, the yield point and modulus of elasticity values for the more rigid and tougher polymer are around 18-20 MPa and

15   2000-3000 MPa respectively.

In the case of other polymers used to obtain the barrier effect (PVA and PGA), the modulus of elasticity is approx. 800 MPa.

Even perishable products such as processed fresh meat, fresh and ripened cheeses and fish are suitably protected against oxidation and aqueous steam

20   transmission.

The film produced according to the process described above therefore consists of a coextruded, multilayer, heat-shrink, weldable  structure with good optical and mechanical characteristics, oxygen and aqueous steam barrier properties, high shrinkage strength and good adherence to the packaged product. The layers also

25   adhere well to one another.

These properties, the list of which is provided by way of example but not of

limitation, in particular define a film for wrapping perishable food and non-food products, which possesses the following characteristics:

- protection against the surrounding environment

- low oxygen and aqueous steam transmission

5   • high mechanical strength

- good weldability

- good presentation of packaged products

- recyclability.

A large-scale trial has been conducted which led to the definition of some specific

10   configurations of laminates that provided very interesting results compared with a high-quality product available on the market .

The polymers used for the trial are normally available on the market. Their trade names are set out in Table 1.

Said specific configurations of laminates are reported in Table 2, while Table 3

15   shows a comparison with a commercial product called BB.

As will be seen from Table 3, said reference film does not curl, because it has a substantially symmetrical structure. In fact, LLDPE (linear low-density polyethylene) has a modulus of elasticity considerably lower than those of the polyamides used in the examples cited, and comparable with that of an ionomer.

20   Conversely, the welding resistance of said film is inferior to that of compositions in accordance with the examples cited.